Inorganic Extraction Studies on the System between Tri-n-butyl Phosphate and Hydrochloric Acid*

By Tomitaro ISHIMORI, Kenju WATANABE and Eiko NAKAMURA

(Received October 28, 1959)

During the course of the solvent extraction studies on fission products and actinide elements with TBP, it was felt that the behavior of other common elements ought to be clarified. In the present paper, is studied the behavior of about fifty chemical elements, ranging from sodium to curium, in the TBP-hydrochloric acid system.

Experimental

Sources of Materials.—Tributyl phosphate was purified in the usual way[1-3], and used without any dilution. Hydrochloric acid solutions were prepared by diluting commercial concentrated hydrochloric acid. The acidity was determined volumetrically if necessary.

Table I[4-8] shows the sources of radioactive tracers. Most of the imported tracers were used as received, whereas Y-90, Nb-95[7] and Ra-224 were prepared from imported Sr-90, Zr-95 and Th-228, respectively. Many other tracers were prepared by irradiating suitable targets in JRR-1. In order to avoid complication as far as possible, very pure materials were used as the targets. The subsequent chemical treatments were carried out if necessary; however, in many cases targets were simply dissolved in acids and converted into chloride solutions.

The radiochemical purities were checked by γ-ray spectrometry, tracing the decay and/or β absorption. Nickel and cadmium tracers contained some radiochemical impurities. Accordingly these tracers were measured at photopeaks using a γ-spectrometer.

---

* TBP

1) K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy and H. A. C. McKay, *Trans. Faraday Soc.*, **52**, 39 (1956).

2) D. F. Peppard, G. W. Mason and J. L. Maier, *J. Inorg. & Nuclear Chem.*, **3**, 215 (1956).

3) D. F. Peppard, W. J. Driscoll, R. J. Sironen and S. McCarty, ibid., **4**, 326 (1957).

4) T. Ishimori, K. Yoshihara and H. Nakamura, 3rd Japan Conference on Radioisotope, S-17 (1959).

5) T. Ishimori, H. Nakamura, and E. Nakamura, ibid., S-16 (1959).

6) N. Shibata and K. Yoshihara, This Bulletin, **32**, 422 (1959).

7) S. Yajima, ibid., **31**, 699 (1958).

8) H. Ebihara and K. Yoshihara, ibid., **33**, 116 (1960).

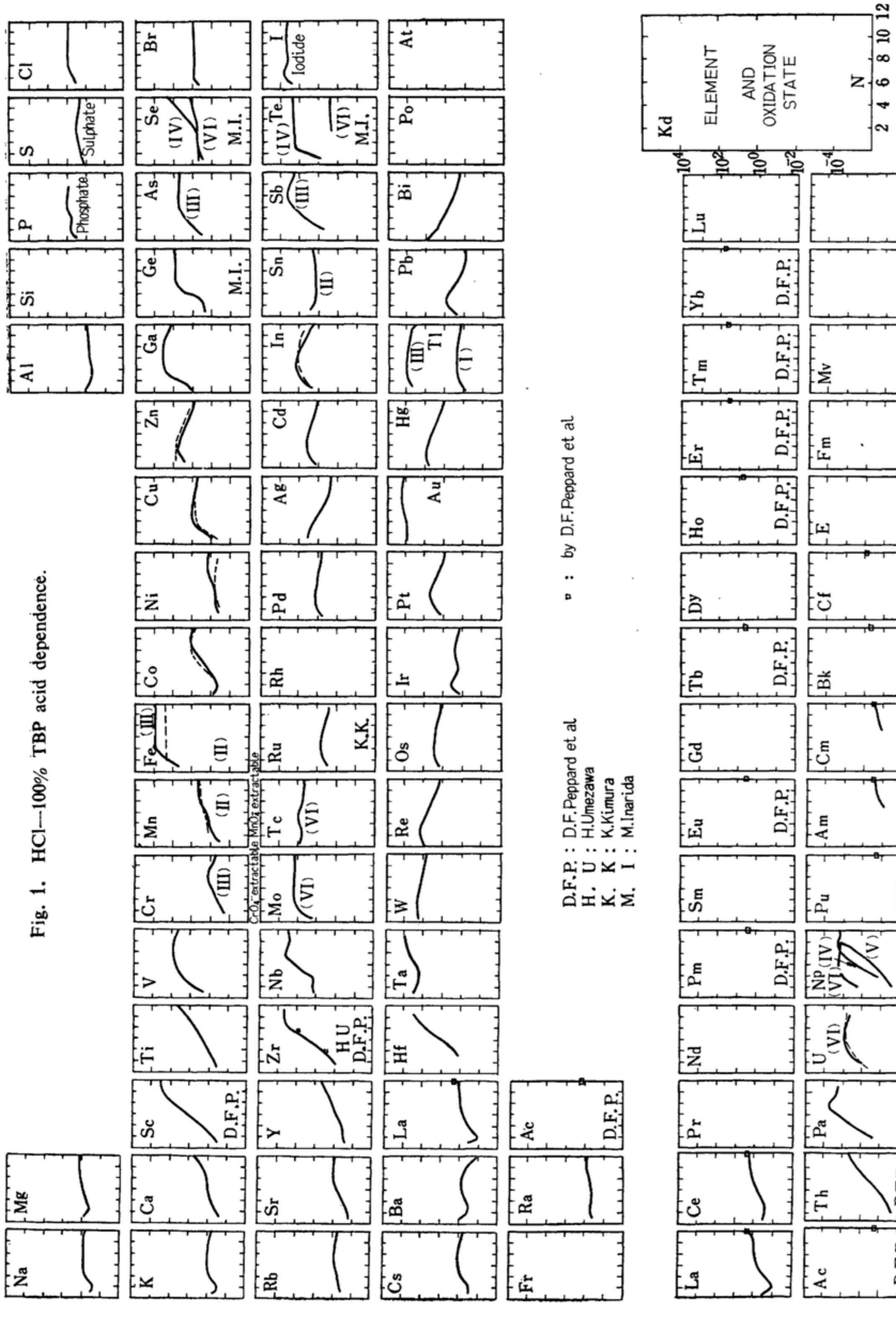

Fig. 1. HCl—100% TBP acid dependence.

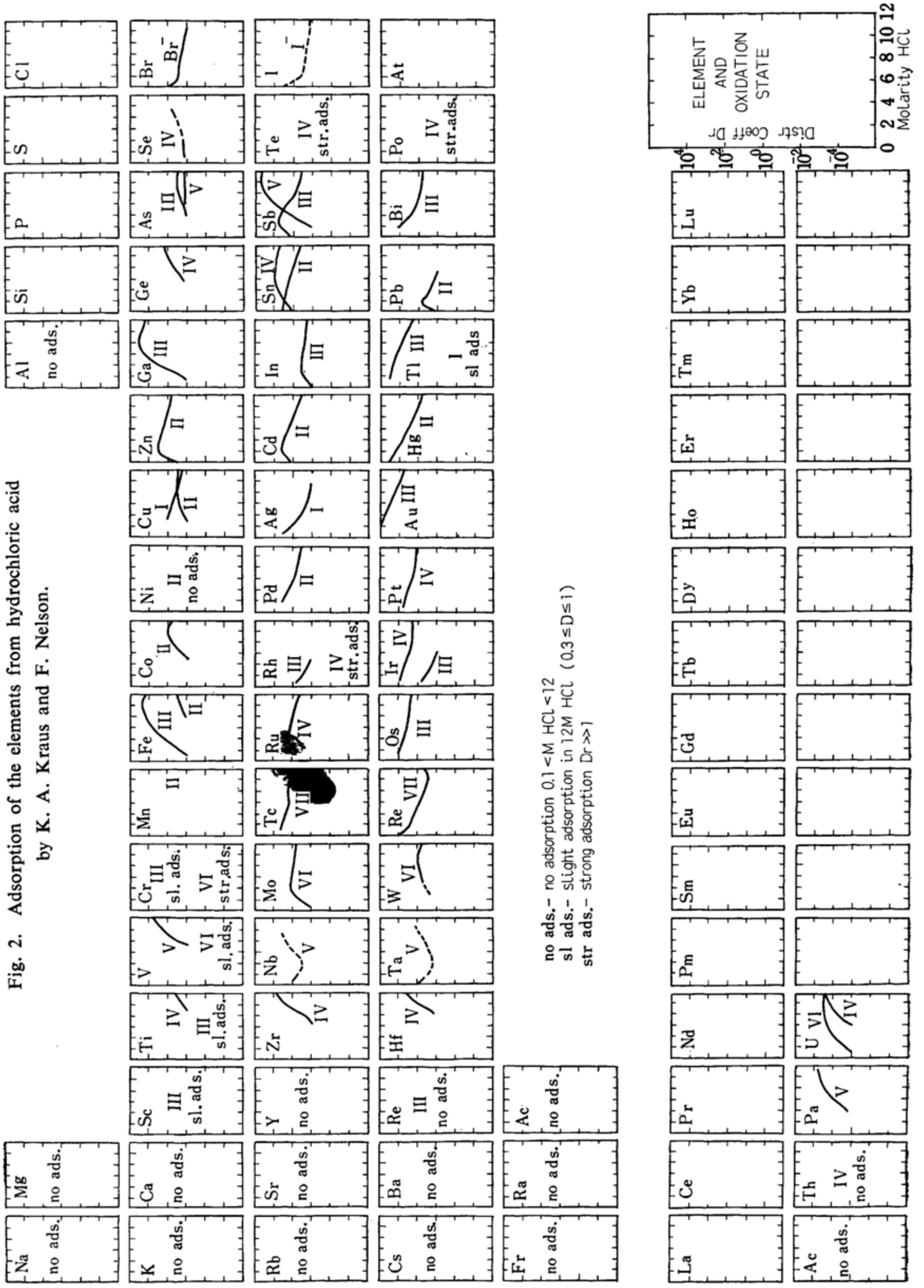

Fig. 2. Adsorption of the elements from hydrochloric acid by K. A. Kraus and F. Nelson.

no ads.- no adsorption $0.1 < M$ HCl < 12
sl ads.- slight adsorption in 12M HCl ($0.3 \leq D \leq 1$)
str ads.- strong adsorption $Dr \gg 1$

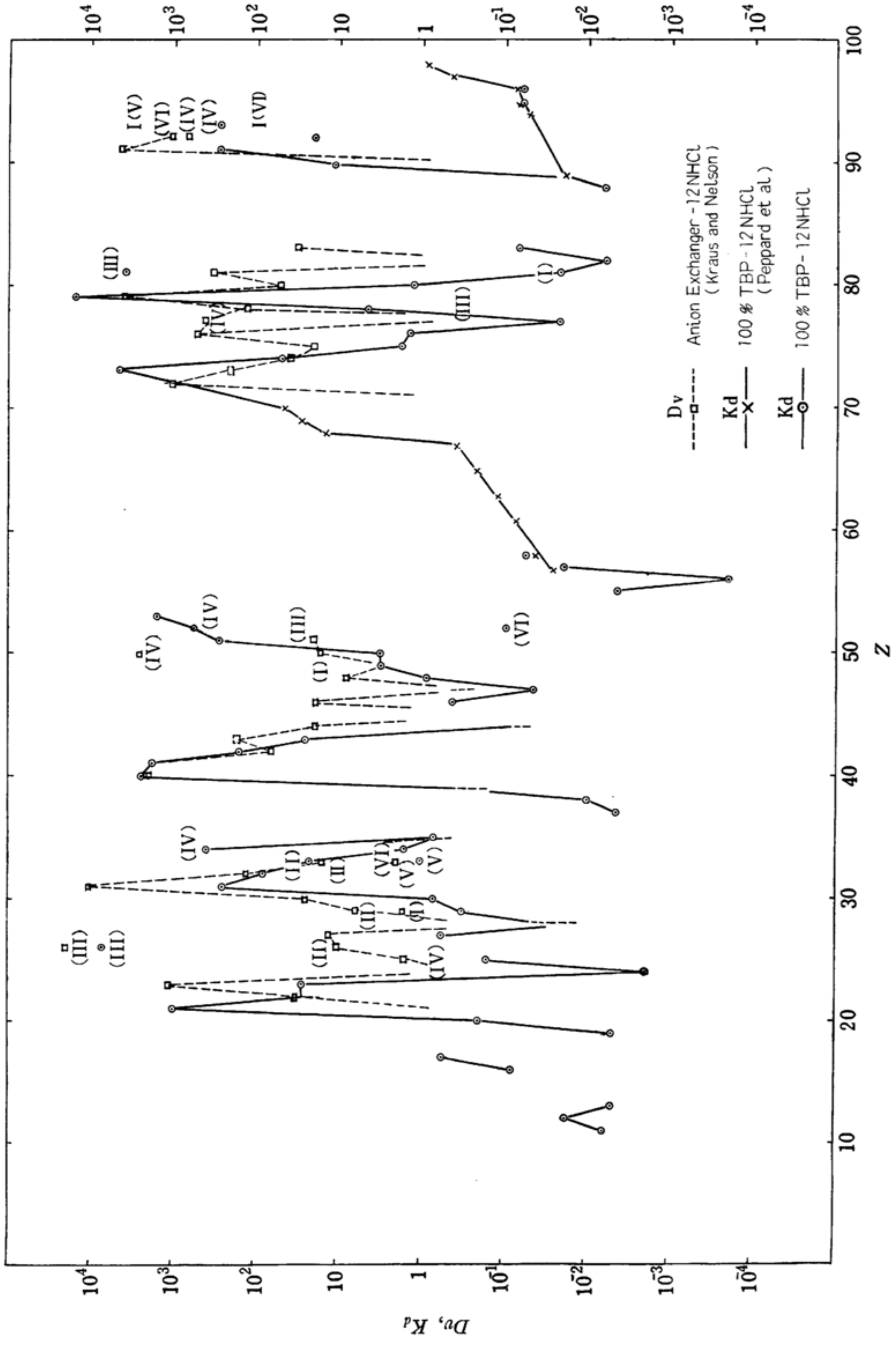

Fig. 3. Solvent extraction and anion exchange at 12 N HCl.

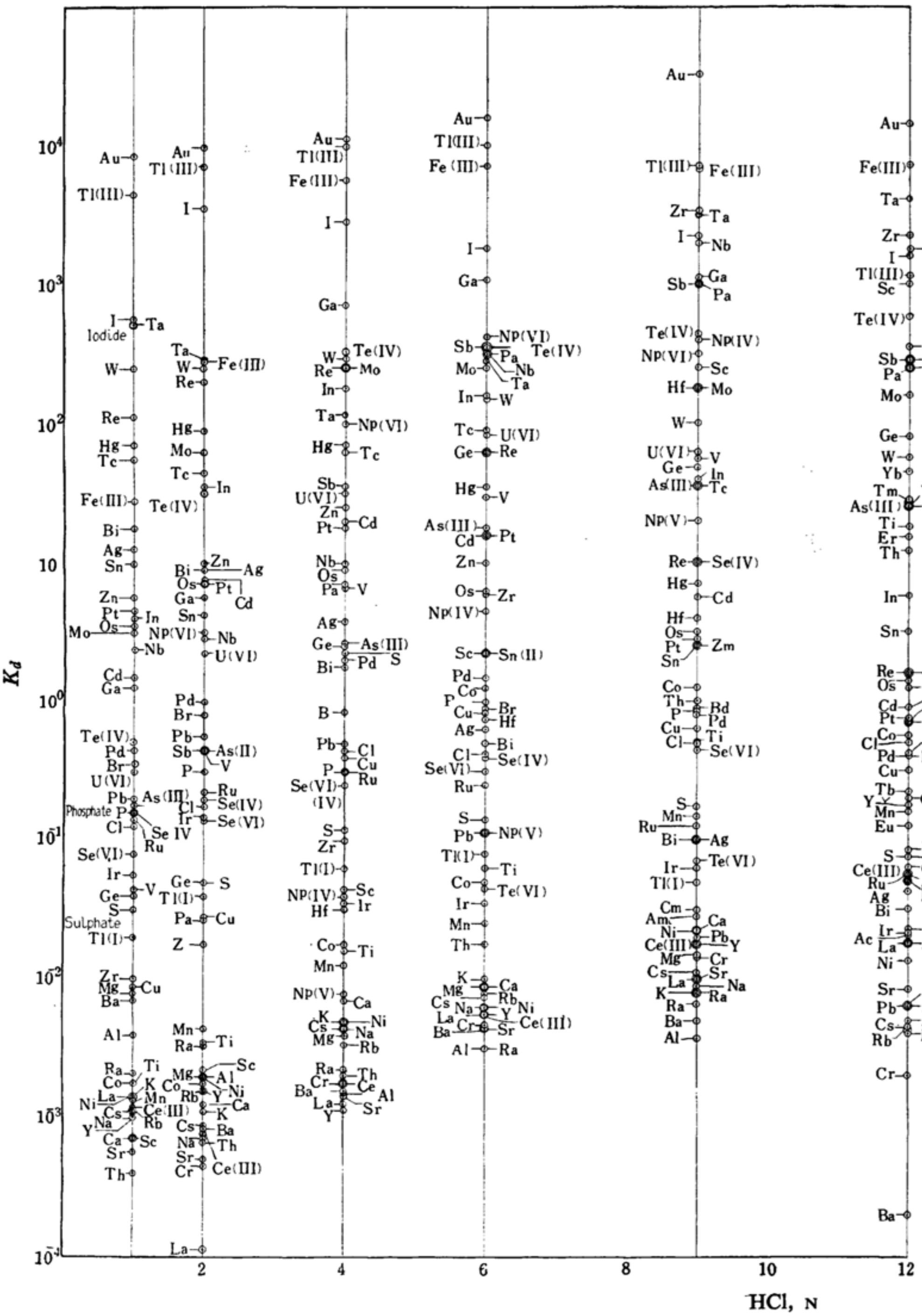

Fig. 4. K_d values in 100% TBP- 1~12 N HCl.

TABLE I. SOURCES OF RADIOACTIVE TRACERS USED

Element	Tracer	Target	Radiochemical purity was checked by	Remarks
Na	Na-24	Na_2CO_3	γ-spectrum, β-decay	
Mg	Mg-27	Mg metal	γ-decay	
Al	Al-28	Al metal	γ-decay, γ-spectrum	
P	P-32	S	β-decay, absorption	Processed, used as $PO_4$4)
S	S-35	BHC	β-decay, absorption	Processed, used as $SO_4$5)
Cl	Cl-38	NH_4Cl	γ-decay	
K	K-42	K_2CO_3	γ-spectrum, β-decay	Prepared by Isotope Production Group, JAERI
Ca	Ca-45			Imported
Ti	Ti-51	$Ti(OH)_4$	γ-decay	
V	V-52	NH_4VO_3	γ-decay	
Cr	Cr-51			Prepared by Yoshihara6), Isotope Production Group, JAERI
Mn	Mn-56	MnO_2	γ-decay	
Fe	Fe-59			Imported
Co	Co-60			Imported
Ni	Ni-65	$Ni(NO_3)_2$		Counted at 1.49 MeV.
Cu	Cu-64	Cu metal	γ-decay, γ-spectrum	
Zn	Zn-65			Imported
Ga	Ga-72	Ga_2O_3	β-decay, γ-spectrum	
As	As-76	As_2O_3	β-decay, γ-spectrum	
Br	Br-80 m, 82	NH_4Br	γ-decay	
Rb	Rb-86, 88	RbCl	γ-decay	Cl-38 was removed by ion exchange
Sr	Sr-90			Imported
Y	Y-90		β-decay, absorption	Milked from imported Sr-90*
Nb	Nb-95		β-decay, absorption	Milked from imported Zr-95 7)
Mo	Mo-99	$(NH_4)_2MoO_4$	β-decay	
Tc	Tc-99			Imported
Pd	Pd-109	Pd metal	γ-decay	Ag-111 was removed by pptn. of AgCl after addition of Ag carrier
Ag	Ag-108	$AgNO_3$	γ-decay	
Cd	Cd-115	Cd metal	γ-spectum	Counted at 0.5～0.525 MeV.
In	In-116 m	In metal	γ-spectrum, β-decay	Prepared by Yoshihara, Isotope Production Group, JAERI
Sn	Sn-121	Sn metal		
Sb	Sb-122	Sb metal	γ-decay	
I	I-131			Imported
Cs	Cs-137			Imported
Ba	Ba-139	$BaCO_3$	γ-decay	
La	La-140	La_2O_3	γ-decay	
Ce	Ce-144			Imported
Hf	Hf-181			Imported
Ta	Ta-182			Imported
W	W-187, 185	W-oxinate	β,γ-decay	Prepared by Ebihara8), Isotope Production Group, JAERI, hotchemically
Re	Re-186, 188	Re metal	γ-decay	
Os	Os-191, 193	Os metal	γ-decay	
Ir	Ir-192, 194	Ir metal	β,γ-decay	Fused with Na_2O_2
Pt	Pt-193, 197	Pt metal	β,γ-decay	Au-199 was removed*
Au	Au-198	Au metal	γ-spectrum, β-decay	Prepared by Yoshihara, Isotope Production Group, JAERI
Hg	Hg-203			Imported
Tl	Tl-204			Imported
Ra	Ra-224		α-decay	Milked from Th-228*

* Procedures are given in the present paper.

Inorganic extraction,
in 100% TBP—HCl system
TBP extraction of,
Na, Mg, Al, PO_4, SO_4, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce and other rare earth elements, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Ra, Th, Pb, Bi, Ra, Th, Pa, U, Np, Am and Cm

The specific activity of these radiochemical tracers were higher than 10^4 cpm/100 microgram. Although in some cases the oxidation states and the chemical forms of the tracer could not be clearly defined, for the most part familiar chemical forms were chosen as far as possible.

Distribution ratios were determined radiometrically in the ordinary way[2,3,9].

Results and Discussion

The results obtained are summarized in Fig. 1 as a series of graphs of log K_d vs. N HCl, where K_d is the distribution ratio and N the molarity. Fig. 1 was compiled from some published and unpublished results. Curves for scandium[2], zirconium[2], some of the rare earth elements[10,11], thorium[2] and some other actinide elements[10,11] are taken from the work of Peppard and his coworkers. Data for zirconium[12], ruthenium[13], germanium[14], selenium[14] and tellurium[14] are taken from the observations of Umezawa et al., Kimura and Inarida. The curves for lead, bismuth, uranium, americium and curium were obtained by one of the present authors (T. Ishimori) during his stay in the Argonne National Laboratory, Lemont, Ill. U.S.A. Finally the three curves for neptunium (IV), (V) and (VI) are quoted from the previous paper[9]. The curves for iron, cobalt, nickel, copper, zinc, indium and uranyl obtained by Irving et al.[15] are added to Fig. 1 with broken lines. Morris and Bell[16] gave the acid dependence curve for cobalt which coincides with that of the present authors. It is likely that permanganate and chromate have fairly high K_d values. However, their values were not plotted because of the rapid reduction of these ions in the system.

As Fig. 1 shows, the four alkali metal elements behave in a similar way, showing always very low K_d values. Halogen elements keep their K_d values practically constant in the higher acidity range over 4 N. There are some similarities in the shapes of the acid dependence curves for zinc, cadmium and bivalent mercury; ruthenium, palladium, osmium and platinum; and tervalent arsenic and antimony, respectively.

The K_d values of scandium, yttrium and lanthanum increase with their decreasing atomic number, Z, at higher acidity range. A similar relationship is seen more clearly among quadrivalent zirconium, hafnium and thorium. In these cases, the element of smaller Z has higher K_d value. On the other hand, the extractability of alkali metal elements or the group of zinc, cadmium and bivalent mercury, does not depend on the value of Z. Further, K_d values of chloride, bromide and iodide increase with their increasing atomic number.

Fig. 2 gives the adsorption behavior of the elements on an anion exchange resin from hydrochloric acid solutions. The curves in Fig. 2 are rewritten in a similar scale with that of Fig. 1 based on the original figure proposed by Kraus and Nelson[17]. As they did not give distribution coefficients, D_v, less than 1, the curves below $D_v=1$ are not drawn in Fig. 2.

The shapes of the acid dependence curve given in Figs. 1 and 2 are very similar for most elements. The high K_d value of scandium is a rare exception. It is not understandable that the solvent-extraction behavior of tervalent antimony resembles the ion exchange behavior of quinquevalent antimony.

It is likely that the resemblance discussed above shows similar mechanisms of distribution between the anion exchange and the extraction with TBP.

The K_d values at 12 N hydrochloric acid were plotted against the atomic number, Z, in Fig. 3. The figure shows that the K_d values vary regularly to some extent, giving two peaks for one long period of the periodic table. The values for lanthanide and tervalent actinide elements are quoted from the work of Peppard et al.[3,10,11] who found the effect of the half-filled shell in the relationship between K_d and Z.

The broken lines in Fig. 3 show the relationship between D_v values of anion exchange and Z. A close similarity is seen here again between the behaviors of the solvent extraction and the ion exchange.

Fig. 4 gives K_d values in the 100% TBP-hydrochloric acid system. This will be convenient for checking the possibility and efficiency

---

[9] T. Ishimori and E. Nakamura, ibid., 32, 713 (1959).

[10] D. F. Peppard, P. R. Gray and M. M. Markus, *J. Am. Chem. Soc.*, 75, 6063 (1953).

[11] P. R. Gray, unpublished results quoted in E. K. Hyde, "Proceedings International Conference on Peaceful Uses of Atomic Energy, Geneva", Vol. VII, P/728, United Nations Publication, New York (1956).

[12] T. Ishimori, H. Umezawa and K. Watanabe, *J. Atomic Energy Soc. Japan*, 1, 299 (1959).

[13] K. Kimura, unpublished.

[14] M. Inarida, unpublished.

[15] H. Irving and D. N. Edgington, *J. Inorg. & Nuclear Chem.*, 10, 306 (1959).

[16] D. F. C. Morris and C. F. Bell, ibid., 10, 337 (1959).

[17] K. A. Kraus and F. Nelson, "Proceedings International Conference on Peaceful Uses of Atomic Energy, Geneva, 1955", Vol. VII, P/837, United Nations Publication, New York (1956).

of a mutual separation of a couple of elements chosen arbitrarily. These K_d values are found with tracers of fairly high specific activities. Therefore, optimum conditions of a separation found in Fig. 4 will fit farily well in a tracer scale chemical separation; however, some caution must be exercised in macro-scale separations. For example, K_d for silver of more than 10 at 1 N acidity, is not applicable in a macro-scale separation because of the formation of insoluble silver chloride. Some examples are given in the following, showing how to utilize the K_d values obtained.

Applications

a) Preparation of Y-90 (or La-140).—The solvent extraction behavior of strontium, yttrium, barium, lanthanum and iron in the 100% TBP-hydrochloric acid system are given in Fig. 5. The curves of Fig. 5. show that the direct separation of Y-90 (or La-140) from Sr-90 (or Ba-140) is not easy. However, the difference between K_d values for iron and yttrium (or lanthanum) is so great that yttrium (or lanthanum) is separated from iron very easily. Yttrium-90 (or La-140) is separated from Sr-90 (or Ba-140) by the carrying down with ferric hydroxide. The precipitate is dissolved in 3 N hydrochloric acid. The TBP extraction

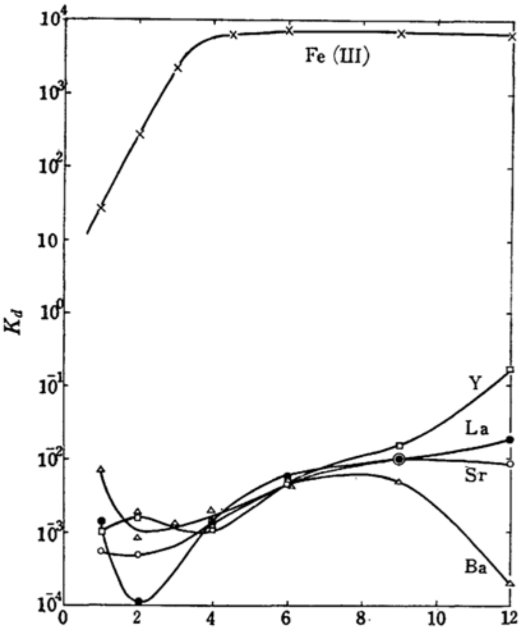

Fig. 5. The K_d valuer of iron, strontium, yttrium, barium and lanthanum.

—×— Fe, —○— Sr, —□— Y,
—△— Ba, —●— La

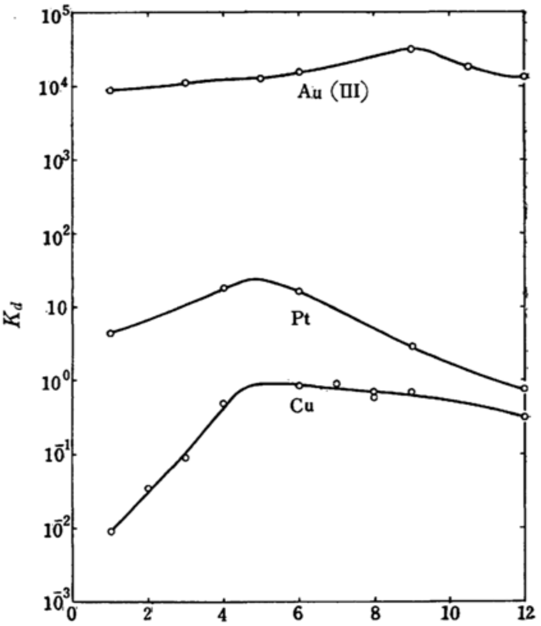

Fig. 6. The K_d values of gold, plutinum and copper.

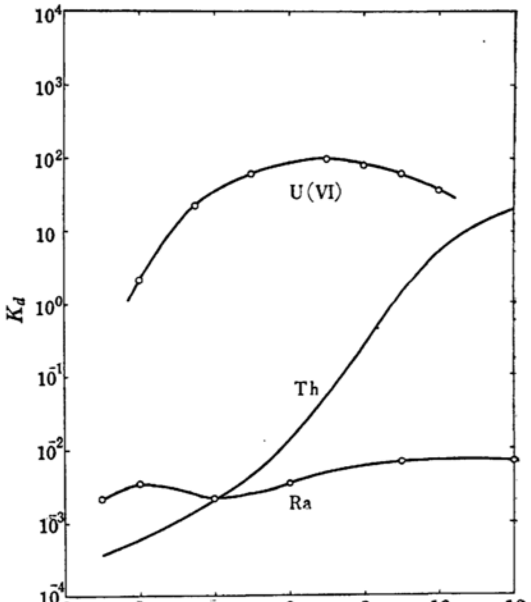

Fig. 7. The K_d values of uranium, thorium and radium in HCl-100% TBP.

The data for thorium was taken from the work of Peppard et al.

removes iron, leaving Y–90 (or La–140) carrier free in the acid solution.

b) Radiochemical Purification of Pt–197.— The difference of K_d values between gold and platinum is shown in Fig. 6. As is seen in the figure, K_d values of platinum are too high to keep platinum in the acid quantitatively. Therefore, TBP is diluted with toluene in order to make K_d values for both elements lower. The TBP (1 : 2) works well for the separation of gold from platinum at 1 or 12 N hydrochloric acid.

Irradiated platinum containing Pt–197 and Au–199 is dissolved in aqua regia, and converted into 1 or 12 N hydrochloric acid solution. Extraction of Au–199 with TBP (1 : 2) brings about an aqueous solution of purified Pt–197 tracer. Gold in copper is removed similarly with diluted TBP from 1 N hydrochloric acid solution. (Fig. 6).

c) Milking of Th-234 from U–238. — The difference between K_d values for thorium and uranyl ion is shown in Fig. 7.

In the 6 N hydrochloric acid—TBP system uranyl ion is extracted into TBP, whereas thorium remains in the aqueous solution. The TBP solution of uranyl chloride is used conveniently as a cow. In this case the addition of a small amount of bromine prevents the photoreduction of uranyl ion.

d) Milking of Ra-244 from Th-228.—As is shown in Fig. 7, radium is not extracted from 12 N hydrochloric acid, while thorium is extractable with a K_d of about 10. Accordingly radium is left in the acid solution after several extractions of thorium with TBP. Both Pb–212 and Bi–212 remain in the acid solution with Ra-224.

Chemistry Division, Tokai Laboratory
Japan Atomic Energy Research Institute
Tokai, Ibaraki-ken